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Title: Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness

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Abstract

Previous laboratory studies have shown reductions in PCB bioavailability for sediments amended with activated carbon (AC). Here we report results on a preliminary pilot-scale study to assess challenges in scaling-up for field deployment and monitoring. The goals of the preliminary pilot-scale study at Hunters Point Shipyard (San Francisco, USA) were to 1) test the capabilities of a large-scale mixing device for incorporating AC into sediment, 2) develop and evaluate our field assessment techniques, and 3) compare reductions in PCB bioavailability found in the laboratory with well-mixed systems to those observed in the field with one-time-mixed systems. In this study we successfully used a large-scale device to mix 500 kg of AC into a 34.4 m² plot to a depth of 1 ft, a depth that includes the majority of the biologically active zone. Our results indicate that after seven months of AC-sediment contact in the field, the 28-day PCB bioaccumulation for the bent-nosed clam, *Macoma nasuta*, field-deployed to this AC-amended sediment was approximately half of the bioaccumulation resulting from exposure to untreated sediment. Similar PCB bioaccumulation reductions were found in laboratory bioassays conducted on both the bivalve, *M. nasuta* and the estuarine amphipod, *Leptocheirus plumulosus*, using sediment collected from the treated and untreated field plots one year after the AC amendment occurred. To further understand the long-term effectiveness of AC as an *in-situ* treatment strategy for PCB-contaminated

sediments under field conditions, a three-year comprehensive study is currently underway at Hunters Point that will compare the effectiveness of two large-scale mixing devices and include both unmixed and mixed-only control plots.

Keywords: Polychlorinated biphenyls; *In-situ* treatment; Bioavailability; Activated carbon; Sediments; San Francisco Bay, USA; Field validation

1. Introduction

Hydrophobic contaminants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dichloro-diphenyl-trichloroethane (DDT), associate with fine-grained, organic-rich, sediment material. This association results in a contaminant reservoir in shallow estuarine and coastal regions from which benthic organisms may accumulate toxic compounds that are then passed up the food chain to fish. Contaminated sediments pose challenging cleanup and management problems, as conventional environmental dredging techniques are expensive, invasive, and sometimes ineffective. *In-situ* treatment strategies may be more effective at reducing risk while decreasing expenditures on sediment management.

In prior research, we observed that PCBs and PAHs in sediment may associated with coal-derived and char particles, in which the compounds are strongly bound and therefore less bioavailable (Bucheli & Gustafsson, 2001; Ghosh, Zimmerman, &

Luthy, 2003; Talley, Ghosh, Tucker, Furey, & Luthy, 2002). Building on this observation, we have tested in the laboratory a new concept for *in-situ* sediment management in which activated carbon (AC) is mixed into contaminated sediments to repartition hydrophobic organic compounds and reduce their availability to water and biota. The physicochemical (Zimmerman, Ghosh, Millward, Bridges, & Luthy, 2004; Zimmerman et al., 2005) and biological (McLeod, Van den Heuvel-Greve, Allen-King, Luoma, & Luthy, 2004; McLeod, Van den Heuvel-Greve, Luoma, & Luthy, 2007; Millward, Bridges, Ghosh, Zimmerman, & Luthy, 2005) results of these laboratory tests have been encouraging. For example, when PCB-contaminated sediment collected from South Basin at Hunters Point Naval Shipyard, San Francisco Bay, CA, USA, was contacted with 3.4% (dry weight) AC on a roller for one month, we observed 87% reductions (Zimmerman et al., 2004) in aqueous equilibrium PCB concentrations and up to 84% reductions (McLeod et al., 2007) in the bioaccumulation of PCBs by the clam, *Macoma balthica*. Six months contact with AC reduced aqueous equilibrium concentrations by over 90% (Zimmerman et al., 2004). These promising laboratory results provide us with a strong basis for expanding the scope of our studies to test the AC treatment technology under field conditions.

With assistance from the U.S. Navy, we recently conducted a preliminary treatability study (Smithenry, Cho, Luthy, & Battelle, 2004) at the Hunters Point tidal mudflat in South Basin (Fig. 1) to assess how the AC treatment technology may be applied in the field. This test site was selected for several reasons. First, PCBs are

identified as the major risk driver for South Basin and most of the sediment in this area has PCB concentrations between 1 and 10 mg/kg (Battelle, 2003). Second, Hunters Point sediment sampling and modeling studies (Battelle, Entrix, & Neptune&Co., 2004) indicate that the South Basin area is a net depositional zone and is comprised of cohesive sediments. Third, Sedflume experiments and hydrodynamic modeling indicated that when AC is mixed into the sediment the critical shear stress for erosion is not diminished and that AC will remain in place due to the cohesive nature of the sediment and the slightly depositional nature of the site (Zimmerman, 2004). Fourth, our initial laboratory feasibility studies were conducted with sediments from the site and provide suitable data for comparison of field results. Last, the site managers at Hunters Point have indicated that they are willing to consider the use of this technology in their final remedial decisions.

In our preliminary field study, the goals were to 1) identify, deploy, and test the capabilities of a large-scale mixing device for incorporating AC into the upper sediment layer, 2) develop and evaluate our field assessment techniques, and 3) compare the reductions in PCB bioaccumulation found in the field to those observed in the laboratory. The Aquamog (Fig. 2), a shallow-draft barge with a rotovator attachment owned by Aquatic Environments, Inc. (Alamo, CA, USA), was identified as a device capable of working on the tidal mudflat and suitable for mixing AC into the sediment. A field test deployment of this device was completed at the end of August 2004. In this paper, we present the results of our field test design and place them into the context of the results gained in our laboratory. In addition, we

emphasize the experience gained in scaling up our AC treatment technology from the laboratory to the field and discuss how this knowledge is useful in carrying out a more comprehensive field evaluation.

2. Materials and methods

2.1. Field Methods

2.1.1. Site Description and Plot Locations.

As represented in Fig. 1, the two sediment plots (Plots A and B) were separated by 4 m and were located approximately 30.5 m from the shoreline within the tidal mudflat region of Hunters Point South Basin. This location was selected because it was accessible from the shore for sediment sampling and away from any possible impacts of potential ongoing PCB releases from the landfill on the north side of the cove (Battelle, 2003). The locations of Plots A and B, identified by taking GPS (NAD83) coordinates at the center of each plot, are N 37° 43.328 / W 122° 22.580 and N 37° 43.321 / W 122° 22.579, respectively. Sampling locations in each plot are identified, along with the positioning of the Aquamog, in Fig. 1. The plots were made to be wedge-shaped to fit the radial operation of the rotovator attachment on the Aquamog. Plot A was selected for AC amendment, while Plot B served as an unmixed control.

2.1.2. Experimental Design.

The overall experimental design for the field test involved two wedge-shaped sediment plots at Hunters Point, each having a surface area of 34.4 m² and an approximate total PCB concentration of 2 mg/kg, which is an average concentration down to 1 ft depth. After the Aquamog was mobilized to the plots in late August 2004, it was used to amend Plot A with a 3.4 dry wt.% AC dose down to 1 ft, corresponding to the biologically active zone. Plot B remained untreated, serving as a spatial control. The activated carbon, TOG[®]-NDS 50×200, was purchased from Calgon Carbon (Catlettsburg, KY, USA), having a particle size range of 75 μm to 300 μm. One month before AC treatment occurred with the Aquamog, both plots were assessed at five sampling locations for 1) amount of total organic carbon (TOC), 2) total PCB concentrations in the 0-1 ft sediment horizon, 3) 28-day PCB bioaccumulation in *Macoma nasuta*, and 4) 28-day PCB uptake into semipermeable membrane devices (SPMDs). These assessments are described in further detail below. Five sampling locations were evenly distributed over the plot, each location representing one fifth of the plot in order to provide average values for the plot. One month after AC treatment occurred, the assessments were completed at the same sampling locations. Seven months after the AC treatment, sediment cores were taken for TOC measurement at the same five locations for Plot A while 28-day SPMD PCB uptake and 28-day clam PCB bioaccumulation were assessed at three new locations for both plots. The 7-month post treatment assessment was not originally planned for this study, so fewer sampling locations were reselected for the clam

bioassay and the SPMD assessments to save time and costs. In addition to these four assessments, the water column above Plot A was sampled one day before, immediately after, and one month after AC treatment occurred in order to assess any PCB resuspension that may arise due to the disruption of sediment consolidation.

2.1.3. Development of Field Sampling Devices.

Besides identifying a mixing device that could incorporate activated carbon into sediment at the field scale, sampling devices used in the laboratory had to be redesigned for use in the field. A depiction of the scale-up that occurred for four field sampling devices is shown in Fig. 3. First, instead of mixing AC into sediment in the laboratory by rolling glass bottles (Fig. 3(A)) for a month or more, AC was distributed in the field onto the sediment surface and then tilled into the sediment for only one half hour using the rotovator on the Aquamog (Fig. 3(B)). As we needed to measure how well the AC was distributed into the sediment, we took sediment cores (Fig. 3(C)) and later assessed the vertical distribution of total organic carbon in the cores. Second, in addition to placing clams into sediment submerged in seawater contained in aerated laboratory aquaria (Fig. 3(D)), in the field we designed 46-cm-long PVC clam tubes with a 15-cm diameter (Fig. 3(E)) that could be pushed into the sediment (Figs. 3(F) & 3(G)). The openings on the sides of the clam tubes allowed for pore water and overlying seawater exchange, while the plastic-coated wire mesh attached to the tube retained the clams inside the tube (clams burrowed to a maximum of six inches) and extending the wire mesh beyond the top of the tube

protected the clams from predators. Third, instead of placing SPMDs into vials containing sediment (Fig. 3(H)) and then rolling them in the lab, SPMDs were suspended vertically inside the clam tube (Fig. 3(I)) to afford sediment contact. Lastly, the effect of AC amendment on sediment stability was assessed in the laboratory through Sedflume studies (Fig. 3(J)); in the field the water column above the sediment plot was sampled through a tube (Fig. 3(K)) and pumped through a filter and resin column (Fig. 3(L)) in order to gauge the amount of suspended solids and PCBs released after AC treatment.

2.1.4. Aquamog Description.

The Aquamog is a barge-like machine with a rotovator attachment typically used to disrupt weed growth in marshy areas. This equipment was identified as being capable of mixing AC into the sediment. A significant feature of the Aquamog lies in its ability to float at high tide (Fig. 2(A)) with minimal draft and settle onto the sediment surface at low tide (Fig. 2(B)). This obviates the possibility of getting stuck in the cohesive sediment. The Aquamog can travel on open water at a few kilometers per hour using its paddling system located in the rear of the barge. Its rotovator attachment is connected to the barge with an arm that has a radial reach of 0.6 m to 5 m from the bow and a side-to-side span of nearly 180 degrees. The attachment is 2 m wide and is connected to the arm at its midpoint. The barge is 3 m wide and 9 m long.

2.1.5. Deployment of Aquamog.

The Aquamog was mobilized at high tide and anchored into position in the front of Plot A at Hunters Point Parcel F. At the beginning of low tide on August 31, 2004, the Aquamog settled onto the sediment surface. At this point, 500 kg of AC were manually poured from 23-kg drums to form an even layer (Fig. 2(B)). This quantity of AC and corresponding surface area were calculated to provide a 3.4 wt.% dry weight AC dose if the Aquamog mixed the AC down to 1 ft. The Aquamog's rotovator was turned at approximately 60 rpm and pulled back and forth across Plot A for approximately 30 minutes until the AC appeared well mixed by visual observation. A picture taken midway through this mixing process is shown in Fig. 2(C). A picture of the final mixed Plot A is shown in Fig. 2(D).

2.1.6. Sediment Core Sampling.

Five, 5-cm diameter sediment core samples were collected from both Plots A and B in order to evaluate average total PCB concentrations in 0-1 ft subsurface sediment and total organic carbon levels before and after AC treatment of Plot A. A sediment PCB concentration for each plot was obtained by averaging of sediment concentrations of five cores ($n = 5$). In previous tests, we found total organic carbon (TOC), as measured by elemental analysis, to be an effective indicator for the amount of AC mixed in the sediment (Smithenry et al., 2004). The core samples were taken to a minimum depth of 1 ft in 50-cm-long cellulose acetate butyrate core liners purchased from Wildlife Supply Company (Buffalo, NY, USA). Sediment

cores were collected, capped, and stored in a 4 °C cold room until they were processed.

2.1.7. Clam Deployment.

In an attempt to measure clam PCB bioaccumulation in the field, five *M. nasuta* with shell lengths between 3.0 and 4.3 centimeters were deployed into each of the mesh-covered 15-cm diameter PVC tubes driven into each plot before and after the AC treatment. These clams, which are native to the San Francisco Bay, were field-collected at Dillon Beach, CA, USA by Aquatic Research Organisms (Hampton, NH, USA). Background PCB levels in these clam tissues were below detection limits (0.01 ppb). Clams were placed onto the sediment surface within each tube's diameter and allowed to burrow. Clams that did not burrow within one day were replaced. After a 28-day exposure, the clams were removed by carefully scooping out the sediment inside the tubes. Clams were separated from the sediment, rinsed with site water, placed in polyethylene containers and transported to the laboratory in a cooler for further processing.

2.1.8. SPMD Sampling.

Before and after AC treatment, an SPMD was deployed inside each of the clam tubes in each plot. The SPMDs are biomimetic devices that passively measure PCB uptake. The SPMDs were custom-made by Environmental Sampling Technologies (St. Joseph, MO, USA) to be 10 cm long and contain 0.1 g triolein, a surrogate for

fish lipid. The SPMDs were vertically suspended inside each clam tube onto two hooks mounted on the inner wall with the top hook three centimeters below the sediment surface. This design allowed the SPMD to be suspended and stretched vertically, keeping it away from the clam tube wall. After a 28-day exposure, the SPMDs were removed, rinsed with deionized water, placed into 100-mL wide-mouth glass bottles with Teflon-lined caps, and stored in a 4 °C cold room until they were processed.

2.1.9. Water Column Sampling.

It was expected that the potential for increased resuspension of sediments and PCBs, if any, would be the greatest as the first high tide covered the exposed Plot A. Thus, overlying water was sampled in duplicate during the first incoming high tide following AC treatment. For comparison, overlying water above Plot A was also sampled during the incoming high tide one day before and one month after the AC treatment. The sample collection apparatus is shown in Fig. 3(L). Sampling involved pumping 40 L of water through Teflon tubing to a glass-fiber filter contained in a stainless-steel filter holder to trap suspended particles and then passing the filtered water through a XAD-2 resin trap in a glass column to measure dissolved PCBs. The method is similar to the surface water sampling method used in the US EPA Lake Michigan Mass Balance Study (<http://www.epa.gov/glnpo/lmmb/methods/>). Some modifications were made to the method to suit the unique field conditions of the sampling. Due to the shallow water over the treatment plot, a peristaltic pump was

used to deliver the water to the in-line filter holders and XAD traps. Teflon tubing was used to collect water samples and was pre-equilibrated with field water by passing about 5 L of water before the start of PCB sampling. The inlet of the Teflon sampling tube was tied to stakes, positioned at 15 cm above the sediment surface, located at the center of Plot A, and remained submerged under water during high tide. The water sample was passed through pre-combusted glass fiber filters with a nominal pore size of 0.7 microns, and then through a pre-cleaned XAD-2 resin adsorbent column. The filter and resin media were prepared for sampling following the method used in the US EPA Lake Michigan Mass Balance Study. The clean filters were wrapped in clean aluminum foil and stored in polyethylene bags until used. After sampling, the filter papers were folded into quarters and stored in clean 250-mL wide-mouth glass bottles with Teflon-lined caps. The ends of the XAD columns were closed using Teflon-lined nylon end-caps during transport before and after sampling. The filter papers containing suspended particulates and the XAD-2 resin columns containing trapped dissolved PCBs were stored at 4°C until they were later processed.

2.2. Laboratory Methods

2.2.1. Core Sampling and Total Organic Carbon (TOC) Analysis.

To assess the depth and homogeneity of the AC mixed in the sediment, each 1 ft sediment core samples was divided into six core cross sections of 2-inch lengths.

Each cross section was homogenized by stirring manually with a stainless-steel spatula, and then approximately 1 g of sediment was subsampled for elemental analysis. These subsamples were dried and ground using an agate mortar and pestle. Approximately 4 mg of each subsample was weighed into a silver boat. Weighed samples were then acidified *in-situ* with 6% sulfurous acid to remove carbonate phases (Verardo, Froelich, & McIntyre, 1990). Each sediment sample was analyzed for total organic carbon (TOC) using a Carlo Erba NA-1500 elemental analyzer. Carbon analysis errors were < 0.5% based on an acetanilide standard (71.1 wt.% C).

2.2.2. Sediment Extraction.

After TOC subsamples were removed, the remainder of the six cross sections from each core was homogenized and a 10-g portion of sediment was removed to measure total sediment PCB concentrations. After drying and grinding, 3 g of the dried sediment was transferred to a 50-mL beaker. Sediment samples were extracted with sonication in a 50% acetone and 50% hexane mixture, following a procedure based on US EPA Method 3550B. The extract was concentrated using a nitrogen blow-down apparatus before cleanup.

2.2.3. SPMD Extraction.

After retrieval, the SPMDs were cleaned by rinsing with deionized water, swirling for 30 seconds in 1 M hydrochloric acid, rinsing with the series of deionized water, acetone, and isopropyl alcohol, and air-drying for approximately 30

seconds. The SPMDs were then submerged in approximately 125 mL of hexane and dialyzed at room temperature for 24 h. The dialysate was removed, and dialysis with fresh hexane was repeated for 8 h. Dialysates were combined with hexane rinse, the total volume was recorded, and aliquots were taken for cleanup.

2.2.4. Tissue Extraction (*Field Deployed Clams*).

After clams were transferred to the laboratory, clams were depurated for 48 hours in clean sediment that was collected from Palo Alto Baylands Nature Preserve, Palo Alto, CA, USA. After depuration, the clams were sacrificed by first opening the shell with a scalpel. Excess water on the inside of the clam was drained by tilting each shell and contacting it with a dry paper towel. The wet tissue was then removed with the scalpel, immediately frozen and stored at -15 °C. The tissue samples were shipped overnight (on dry ice in a cooler) to Battelle Duxbury Operations for tissue analyses. The analysis of PCBs was performed according to low-level methods developed for the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program (Lauenstein & Cantillo, 1993), as described in BDO SOP 5-190 (Battelle Duxbury Operations). Upon arrival, the tissues were homogenized by macerating the tissues using a Tekmar tissuemizer (Tekmar, Cincinnati, OH, USA) and 75 mL of dichloromethane (DCM) until uniform slurries were attained. This procedure was repeated once and the extracts decanted between tissumizing steps. A third extract was accomplished by adding 50 mL of DCM to the tissue in the extraction vessel and shaking for 0.5 hours. A 10-mL portion of the extracts was

air-dried to determine the DCM-extractable lipid concentration. The remaining portion of extracts was solvent exchanged into hexane prior to PCB congener analyses.

2.2.5. Laboratory PCB Bioaccumulation Assays.

In addition to the *M. nasuta* deployed in the field, further PCB bioaccumulation studies were conducted in the laboratory with *M. nasuta* and *Leptocheirus plumulosus* using the sediment collected from Plots A and B in Hunters Point South Basin one year after AC treatment occurred. Sediment samples from the field were not homogenized for use in the laboratory trials in order to preserve field conditions as closely as possible. Cakes of sediment with an approximate depth of 6 inches were taken, directly placed into 20-L buckets, and moved to the laboratory. Subsamples of the sediment were sent to the U.S. Army Engineer Research and Development Center (U.S. Army ERDC) for the *L. plumulosus* bioassays and the remaining sediment was transferred into 2-L beakers with a diameter of 14 cm, a similar width to that of PVC clam cages for *M. nasuta*.

In the 28-day laboratory exposures, *M. nasuta* with shell lengths between 2.5 and 3.3 centimeters (Aquatic Research Organisms, USA) were placed in the beakers in which the contained sediment had been previously submerged in aquaria containing 31‰ filtered seawater (Long Marine Lab, Institute of Marine Sciences, University of California Santa Cruz, USA) at 15 °C. Four replicates containing six clams each were performed for each sediment sample. The seawater was aerated gently and

exchanged once a week. After 28-day exposures, clams were depurated for 24 hours in clean sediment (collected from Palo Alto Baylands Nature Preserve, Palo Alto, CA, USA) and then 48 hours in seawater prior to being sacrificed. The procedure of clam sacrificing was the same as described in the previous Section 2.2.5. The tissues were stored at -15 °C.

Three replicates of *L. plumulosus* were exposed to sediment from each plot using procedures described by Millward et al (Millward et al., 2005). Briefly, wet sediment was added to each replicate 1-L beaker on a 100 g dry-weight basis. Each beaker contained 25 juvenile amphipods exposed to sediments for 28 days at 25.0 ± 1.0 °C using 20‰ reconstituted seawater (Crystal Sea Marine Mix, Marine Enterprises International, Baltimore, MD, USA) as overlying water. After 28 days of contact, the amphipods were removed from the sediment and allowed to clear gut contents for 2-4 hours before being placed in storage at -80 °C.

2.2.6. Tissue Extraction (Laboratory Bioaccumulation Studies)

Of the six whole clam tissues obtained from each replicate exposure, three were selected at random, frozen at -80 °C for 24 hours, and freeze-dried (VirTis® Benchtop 4K Freeze Dryer model 4KBTXL-75, Gardiner, NY, USA) for three days. The three dried tissues of each replicate were then combined, crushed, and homogenized to fine powder. From the resulting homogenate for each replicate, a subsample was taken to a 50-mL beaker and the weight was recorded. After spiking the subsample with 10 µL of analyte surrogate (PCB 14 and PCB 65), it was

extracted three times with sonication in 20 mL of DCM, following a procedure based on US EPA Method 3550B. The solvent of the extract was exchanged to hexane using a nitrogen blow-down apparatus and the extract was concentrated before cleanup. Amphipod tissues were extracted as described by Millward et al (Millward et al., 2005) using a modified US EPA method 3550B adapted for small wet weights of tissue (~100 mg).

2.2.7. XAD-2 and Filter Extraction.

The XAD-2 resin and the glass fiber filters were extracted in a soxhlet extraction system with a 50% acetone and 50% hexane mixture. The soxhlet extraction procedure followed US EPA method 3540C. The extract was concentrated in a rotary evaporator (Buchi SafetyVAP model R200A, Buchi, Switzerland) and a nitrogen blow-down apparatus (N-evap model 250G, Organomation Inc, Berlin, MA) before cleanup.

2.2.8. Extract Cleanup.

Extracts obtained from SPMDs, sediment, XAD-2 resin, and glass fiber filters were cleaned from organic interferences using a deactivated silica gel column following US EPA method 3630C. Extracts from the field deployed clam tissues were cleaned through an alumina column, concentrated, and further purified by gel permeation column/high performance liquid chromatography (GPC/HPLC) as described by BDO SOP 5-128 following the NS&T methods (Lauenstein and

Cantillo, 1993). Clam tissue extracts obtained from the laboratory bioaccumulation study were cleaned via sulfuric acid/potassium permanganate and then eluted through a deactivated silica/alumina column (Lauenstein & Cantillo, 1993; USEPA, 2000). Sulfur interferences were removed by contacting with activated copper following EPA method 3660B. Amphipod tissue extracts were cleaned and concentrated down to 40 μL as described by Millward et al (Millward et al., 2005) using US EPA method 3630C.

2.2.9. PCB Analysis.

PCB congeners in extracts from field-deployed clam tissues were measured following BDO SOP 5-182 using an Agilent 6880 gas chromatography/electron capture detector (GC/ECD) (Battelle Duxbury Operations). This protocol determined the concentrations of eighteen PCB congeners. In the case of laboratory-deployed clam tissues, SPMDs, sediment, XAD-2, and glass fiber filters, US EPA Method 8082 was applied to analyze PCB congeners in extracts obtained from those samples. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm ID) and a micro electron capture detector was used for analysis. A 5-level PCB calibration table was prepared using a known PCB mixture containing 250 $\mu\text{g/L}$ of Aroclor 1232, 180 $\mu\text{g/L}$ of Aroclor 1248 and 180 $\mu\text{g/L}$ of Aroclor 1262 yielding a total PCB concentration of 610 $\mu\text{g/L}$. The known PCB calibration mixture was obtained from the US EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan. Concentrations

of individual PCB congeners in the mixture were obtained from Mullin (Mullin, 1994). Two internal standards were used: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, ninety-two PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks are calibrated as the sum of congeners. PCB analysis of amphipod tissues was done as reported by Millward et al (Millward et al., 2005) using US EPA method 8270 and selective-ion monitoring on a Hewlett-Packard 5890 series II gas chromatograph-mass spectrophotometer. Seventeen congeners or coeluting peaks were analyzed and summed to give a total PCB level in a sample.

3. Results and Discussion

3.1. Homogeneity of AC Mixing.

A spatial representation of the TOC results for Plot A before and after AC mixing treatment is given in Fig. 4. This representation indicates that 1) the amount of carbon in Plot A increased after AC treatment, and 2) some areas of Plot A had more homogenous AC mixing than others. The low standard deviations among the core cross sections for Cores 4 and 5 indicate that the Aquamog did the best mixing near its bow. In fact, the average TOC values for two well-mixed cores (Core 4:

3.7% \pm 0.4 and Core 5: 4.2% \pm 0.5) match well with the expected value of 3.8 wt.% C for a 3.4 wt.% AC dose to this sediment. The expected value was calculated as follows: if 3.4-g AC (TOC = 86.1%) is added to 100-g Plot A sediment (TOC = 1.0%), then the resulting 103.4-g mixture would contain a total 3.93-g TOC (3.8%). As the rotovator moved farther away from the bow, the mixing was less homogeneous, with fair mixing occurring at Cores 2 and 3 and poor mixing near Core 1. As expected, when sediment cores taken from Plot A seven months after AC treatment were analyzed for TOC, no significant differences in the AC amount at the individual sampling locations were found when the TOC values between the one- and seven-month samplings were subjected to a paired student's t-test at the 95 percent confidence level. It should be noted that the average TOC values for Plots A (1.0% \pm 0.3) and B (0.7% \pm 0.4) were found to be similar before AC treatment.

3.2. PCB Uptake into SPMDs.

The total PCB uptakes into the SPMDs for Plot A and Plot B throughout three sampling intervals (before AC addition, one month after AC addition, and seven months after AC addition) are shown in Fig. 5. These uptakes were normalized by the different sediment PCB concentrations in Plot A (2100 \pm 300 ng/g) and Plot B (1600 \pm 300 ng/g) sediment concentration of each plot. Whereas the normalized SPMD uptakes in the two plots were not significantly different from each other before AC addition, the AC-treated Plot A showed 34% less SPMD uptake than that

of Plot B one month after AC treatment (t-test, $p = 0.01$). The difference between the two plots increased up to 62% after 7 months of AC-sediment contact (t-test, $p < 0.01$). This suggests that transfer of the PCBs to the AC continued during months 1 to 7 following mixing of Plot A. In comparison, in the laboratory we have observed up to 77% reductions in PCB uptake for SPMDs that had been contacted with well-mixed (six months on a roller) AC-amended Hunters Point sediment (Zimmerman et al., 2005). This difference between field and laboratory SPMD uptake is likely due to the considerable differences in mixing conditions and contact of the AC with the sediment. In the field, the AC was mixed into the sediment for a total of 30 minutes compared to the mixing times in the laboratory of up to six months. Nonetheless, up to 62% of reduction in SPMD uptake in the field is encouraging and leads us to expect further reductions over time as the PCBs continue to repartition into the AC in Plot A. The reduction in SPMD uptake is also significant considering that the mixing of Plot A homogenized the sediment and may have enhanced contact with the SPMD in comparison to the unmixed sediment in Plot B. This last point emphasizes the importance of having a mixing-control plot where the sediment is mixed yet no AC is added. In this way, the impact of mixing can be separated from the variable of AC addition. Mixing control plots have been incorporated into the experimental design for a larger field study that is currently underway at Hunters Point (Smithenry, Cho, & Luthy, 2005). Additionally, we observed some variation of SPMD uptakes from the untreated Plot B among the three sampling points without any noticeable changes of sediment properties. The variability of SPMD

uptakes from Plot B through the sampling period might be due to field condition factors such as tidal pumping, seasonal effect, pore water PCB concentration, and other field factors like sediment structure.

3.3. PCB Bioaccumulation.

As an indication that our clam deployment procedures were effective, and that the AC had no effect on *M. nasuta* mortality, an overall survival rate of 98% was found for the clams retrieved after the 28 days of field exposure. Fig. 6(A) shows the PCB bioaccumulations factors (BAF = tissue concentration/sediment concentration) for field-deployed *M. nasuta* in the AC-treated Plot A and the untreated Plot B for 28-day exposures. The BAFs of Plot A were significantly less compared to Plot B at seven months post-treatment assessment by 53% (t- test, $p = 0.02$). Although the p value for the difference at one month after AC treatment was not less than the 0.05 alpha level ($p = 0.19$), the 24% difference appeared to be reasonable when compared to the difference of PCB uptakes into SPMDs observed at the same time. To consider the possible effect of AC on lipid contents in clams, lipid-normalized BAFs (BAF/lipid content) are also presented (Fig. 6(B)). Similar to the non-normalized BAFs, the lipid-normalized BAFs for clams exposed to AC-amended sediment were significantly less in comparison with untreated sediment at 7-month post assessment (49%, $p < 0.01$). Also, the one-month post assessment gave a 32% difference, although the p value did not indicate significance (t-test, $p = 0.06$). Our small sample

sizes and kinetic factors affecting PCB uptake by the AC in the field likely prevented us from seeing significant differences in the one-month data set.

As expected from the PCB uptakes into the SPMDs in the control Plot B, the BAFs as well as the lipid-normalized BAFs from Plot B were varied even with constant sediment properties during three assessments (one month before, one month after and seven months after AC treatment occurred). Therefore, it is difficult to directly compare the time series BAFs obtained from each plot. Rather, in this study, the spatial control (Plot B) played a prominent role in proving the effectiveness of AC treatment in reducing PCB bioaccumulation in *M. nasuta* as well as PCB uptake into SPMDs.

To ascertain the AC treatment effect on PCB bioaccumulation, another round of PCB bioaccumulation studies with *M. nasuta* and *L. plumulosus* were later conducted in the laboratory with non-homogenized and non-altered sediment collected from both plots one year after AC treatment occurred. As shown in Fig. 7, the BAFs obtained from exposures to Plots A and B indicated the lower transfer of PCB from sediment to clam and amphipod tissues in the AC-treated Plot A sediment. The BAFs were significantly less for both *M. nasuta* (t-test, $p = 0.02$) and *L. plumulosus* (t-test, $p = 0.04$) exposed to the AC-treated Plot A sediment relative to the untreated Plot B sediment, with 51% and 50% differences, respectively. The clam BAF values observed in the laboratory are one order of magnitude larger than those from the field, which are likely due to the different units of the PCB tissue concentrations (wet weight versus dry weight) and the different numbers of PCB

congeners for analyses (18 versus 92). Although there was the possibility during coring and sampling of some inevitable alteration of the sediment state and layered structure, and the surrounding environment, these laboratory results were well matched with the field results for the seven-month post-treatment bioaccumulation. This is believed to provide another line of evidence of AC amendment effectiveness in the field.

As expected from the differences in mixing conditions, the differences in 28-day PCB bioaccumulation (~50%) observed for the one-time-mixed AC-amended sediment obtained from the field were less than the laboratory-scale reductions (~80%) reported (McLeod et al., 2007; Millward et al., 2005) for biota exposed to AC-amended sediment that had been continuously mixed for one month in the laboratory. Nevertheless, the 50% difference in PCB bioaccumulation is striking for a one-time-mixed system under field conditions as it suggests that significant reductions can occur at time scales that are relevant to field remediation efforts. The PCB bioaccumulation differences found between this system mixed for 30 minutes versus those mixed for one month are in line with the modeling efforts that describe of the aqueous PCB concentrations in one-time-mixed AC-amended sediment systems (Werner, Ghosh, & Luthy, 2006). According to this model, after five or more years of AC-sediment contact, the reductions in aqueous PCB concentrations observed for one-time-thoroughly-mixed systems (field) may approach those found for systems mixed for extended periods in the laboratory. Indeed, this convergence is not surprising when one considers that the majority of PCBs discharged into Hunters

Point South Basin sediment between 1954 and 1974 had migrated to the char and coal-derived particles (Ghosh et al., 2003) that were introduced into the sediment through historic anthropogenic activities. With these ideas in mind, we anticipate that PCBs will continue to be repartitioned in the field and that this mass transfer process will be augmented by bioturbation, wave action, and tidal pumping. Therefore, we project that further reductions in bioaccumulation will be observed in the field over time, as we already observed within relatively short periods (one month to seven months).

3.4. PCB Resuspension in Water Column.

As shown in Fig. 8(A), the average total PCB concentrations in the aqueous phase above Plot A were similar one day before, immediately after, and one month after mixing AC into sediment. This shows that the AC amendment and mixing resulted in no measurable release of PCBs into the water column. Likewise, as shown in Fig. 8(B), there was essentially no increase in PCBs associated with suspended particles in the water column observed during the first high tide immediately after AC treatment. There was a large increase in suspended particle-associated PCBs during the third sampling event one month later. This increase is attributed to wind-induced turbulence.

Average wind speed and wind direction during the sampling times were calculated based on available surface weather observation data from the nearest

National Oceanic and Atmospheric Administration (NOAA) monitoring station at San Francisco Airport. Average wind speeds during the sampling periods for the three days (D1: one day before, D2: immediately after, and D3: one month after AC treatment) were 9.0, 9.6, and 12.1 km/hr, respectively. Wind gusts of 24 km/hr were also registered on D3. Thus, there was an increase in wind speed during the sampling times on D2 and D3. Wind direction was also different on the three sampling days. Average wind direction was 310, 270, and 250 degrees on D1, D2, and D3, respectively. Thus, D1 wind would have blown along the shoreline, while D3 wind would have blown from the center of the basin towards land. The large increase in D3 wind speed and the change in wind direction likely increased the sediment resuspension on that day. This increase in sediment resuspension was confirmed through estimates of suspended solids concentrations obtained from the dried filter papers: 12 mg/L on D1, 22 mg/L on D2, and 36 mg/L on D3. Overall, these results suggest that wind speed and direction have a greater impact on resuspension of particle-associated PCBs than the immediate effect of mechanical mixing of AC with sediment. The observed wind induced effects are likely representative of more basin-wide phenomena than that localized over the relatively small test plots.

4. Conclusion

We recently completed a preliminary study at Hunters Point to assess an *in-situ* mixing AC treatment technology for PCB-contaminated sediment under field conditions. We successfully deployed a large-scale mixing device and used it to amend a sediment plot with a 3.4 wt.% AC dose. Our results show that this device mixed AC homogeneously into most of the sediment plot. The effectiveness of the AC treatment was demonstrated by a series of assessments. In just one month after AC treatment, 34% less PCB uptake into SPMDs and 24% less PCB bioaccumulation in *M. natuta* deployed in the field was found upon exposure to AC-amended sediment in comparison to untreated sediment. Seven months after the AC treatment occurred, the differences further increased up to 62% less in SPMD uptake and 53% less in clam bioaccumulation, which implies the possibility of the long-term effectiveness of AC. Those field results were in alignment with the results of supplementary laboratory bioaccumulation assays, which showed approximately 50% less PCB bioaccumulation in *M. nasuta* and *L. plumulosus* exposed to AC-amended sediment obtained from the field one year after treatment in comparison to untreated sediment. Further reductions in PCB bioaccumulation are expected in the field as the contact time between AC and sediment increases. The knowledge and experience gained in this preliminary study is currently being applied to a larger field study that began in 2006 (Smithenry et al., 2005). The main goal of this more comprehensive field study, which will compare two mixing devices and comprise unmixed and mixed-only control plots, will be to further understand the long-term

effectiveness of AC as an *in-situ* treatment strategy under field conditions for PCB-contaminated sediments.

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Figure captions

Fig. 1. Schematic of (A) San Francisco Bay; (B) Hunters Point Naval Shipyard and South Basin; (C) Plot A, Plot B, and Aquamog; and (D) five sampling locations in each plot.

Fig. 2. (A) Mobilizing Aquamog to Plot A at high tide; (B) before, (C) during, and (D) after mixing activated carbon into sediment.

Fig. 3. Comparisons of laboratory and field techniques for assessing (A)–(C) AC mixing, (D)–(G) PCB bioaccumulation in clams, (H)–(I) PCB uptake in SPMDs, and (J)–(L) stability of AC-treated sediment.

Fig. 4. Comparison of TOC values from sediment cores taken before and after AC treatment in Plot A.

Fig. 5. Comparison of PCB uptakes into SPMD normalized by sediment PCB concentration exposed to the AC-treated Plot A and the untreated Plot B sediment for 28 days. Each column and error bar represents the mean and one standard deviation ($n = 3\sim 5$).

Fig. 6. Comparison of bioaccumulation for field-deployed *M. nasuta* for 28 days.

(A) Bioaccumulation factors (BAF = Tissue PCB concentration / Sediment PCB concentration) (B) lipid-normalized BAFs for *M. nasuta* exposed to the AC-treated Plot A and the untreated Plot B sediment. PCB tissue concentrations are based on wet weight. Each column and error bar represents the mean and one standard deviation (n = 3~5).

Fig. 7. Comparison of bioaccumulation factors for *M. nasuta* clams and *L.*

plumulosus amphipods exposed to the AC-treated Plot A and the untreated Plot B sediment for 28 days in laboratory tests with field cores collected one year after treatment. PCB concentrations in *M. nasuta* tissue are based on dry weight; *L. plumulosus*, wet weight. Each column and error bar represents the mean and one standard deviation (n = 4).

Fig. 8. Comparison of (A) aqueous PCB concentration and (B) particle-associated PCB concentration sampled above Plot A during high tide one day before, immediately after, and one month after AC treatment. Each column and error bar represents the mean and one standard deviation (n = 2).

Fig. 1

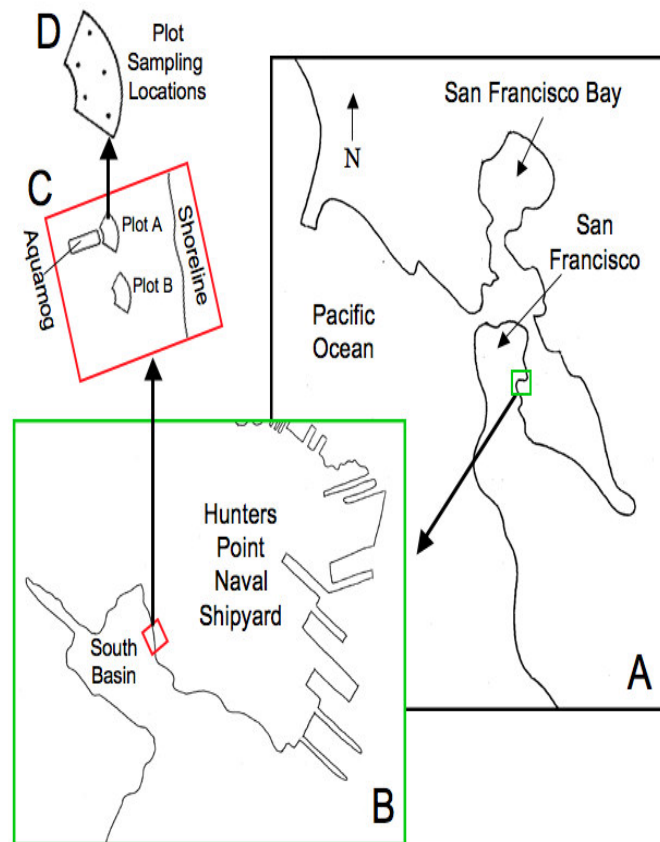


Fig. 2

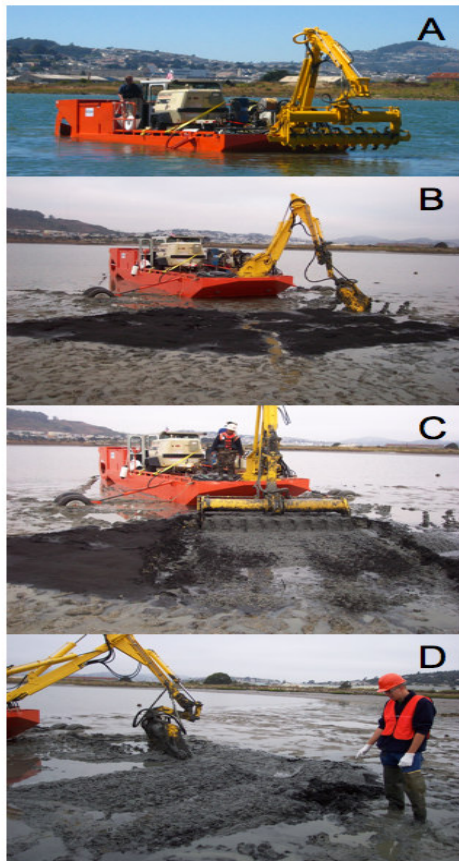


Fig. 3

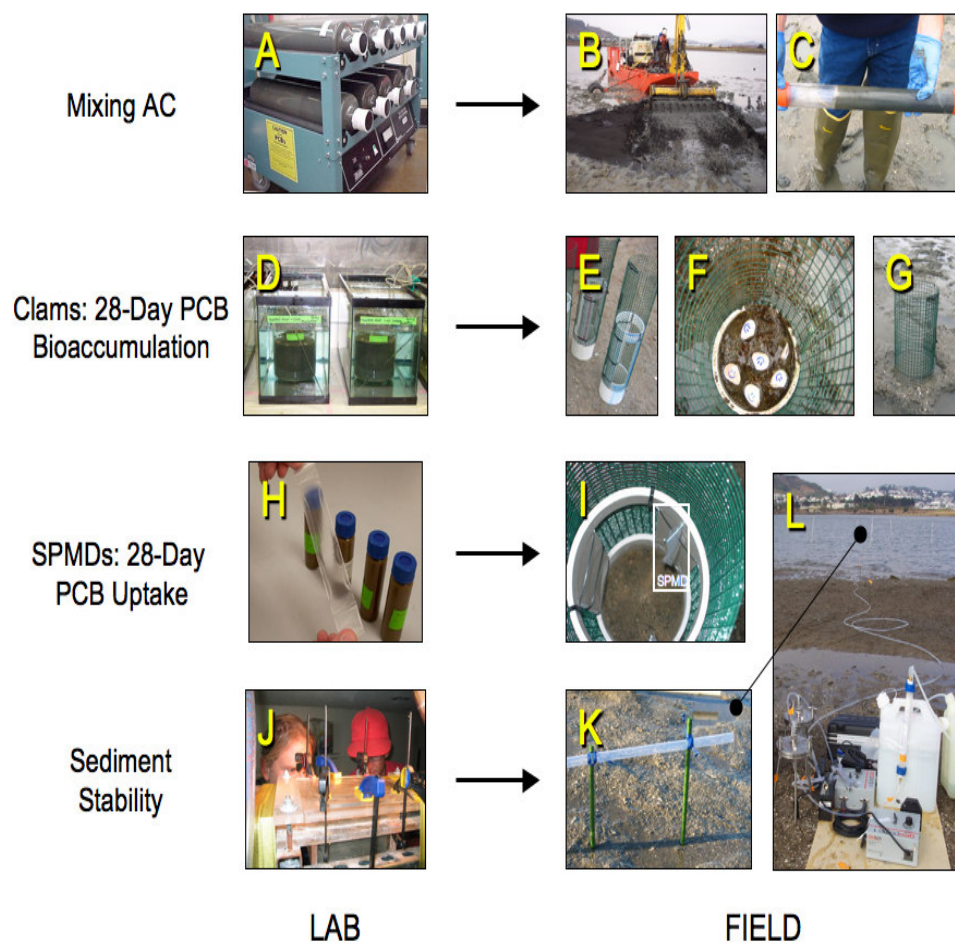


Fig. 4

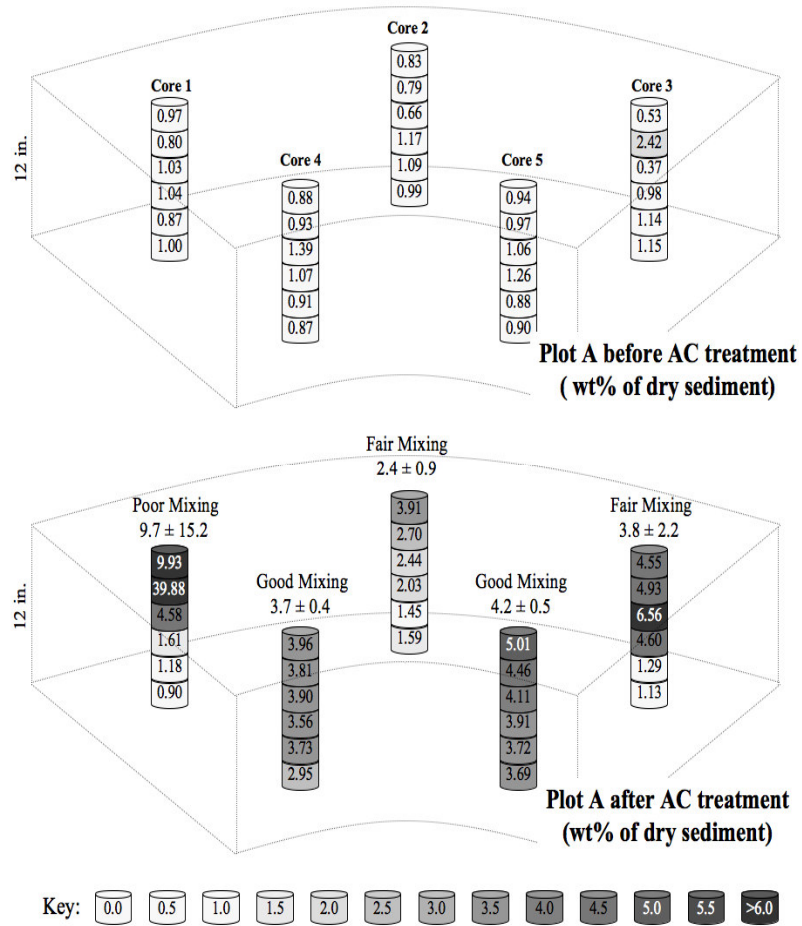


Fig. 5

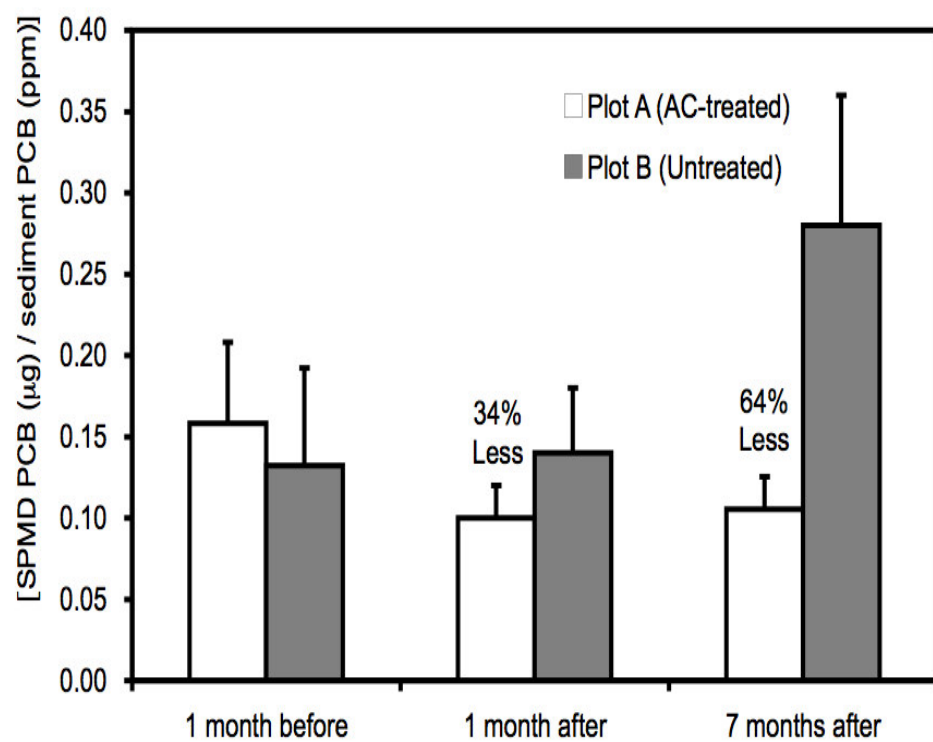


Fig. 6

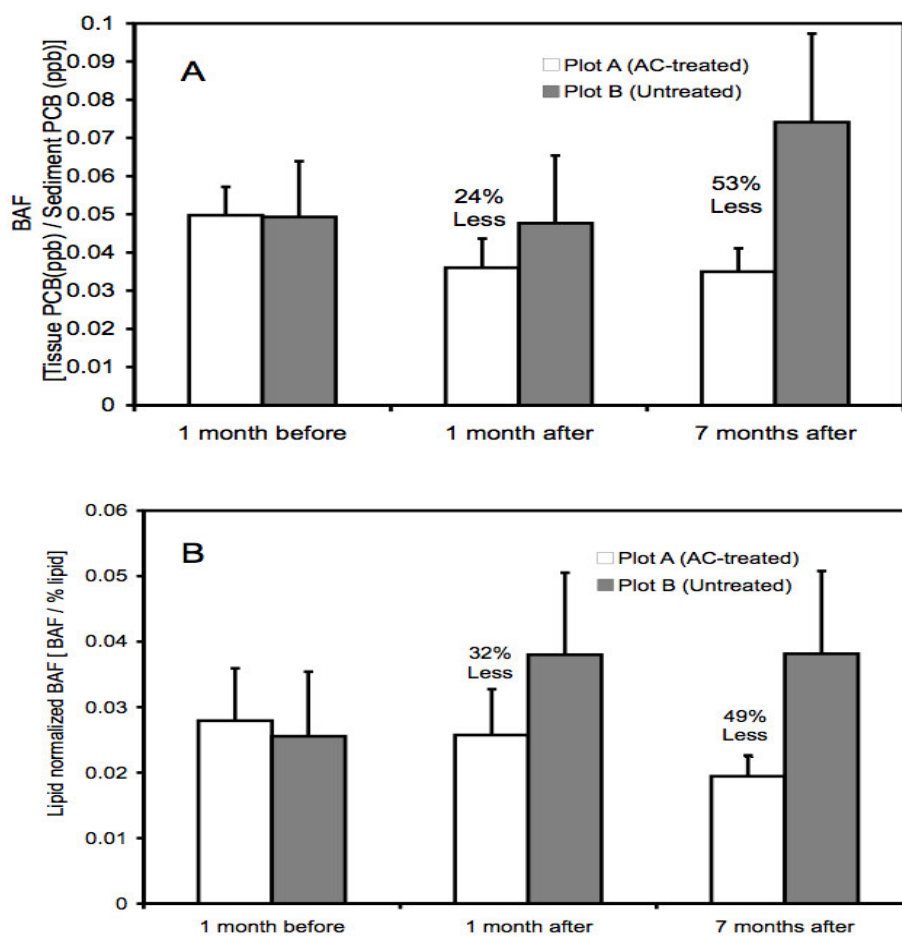


Fig. 7

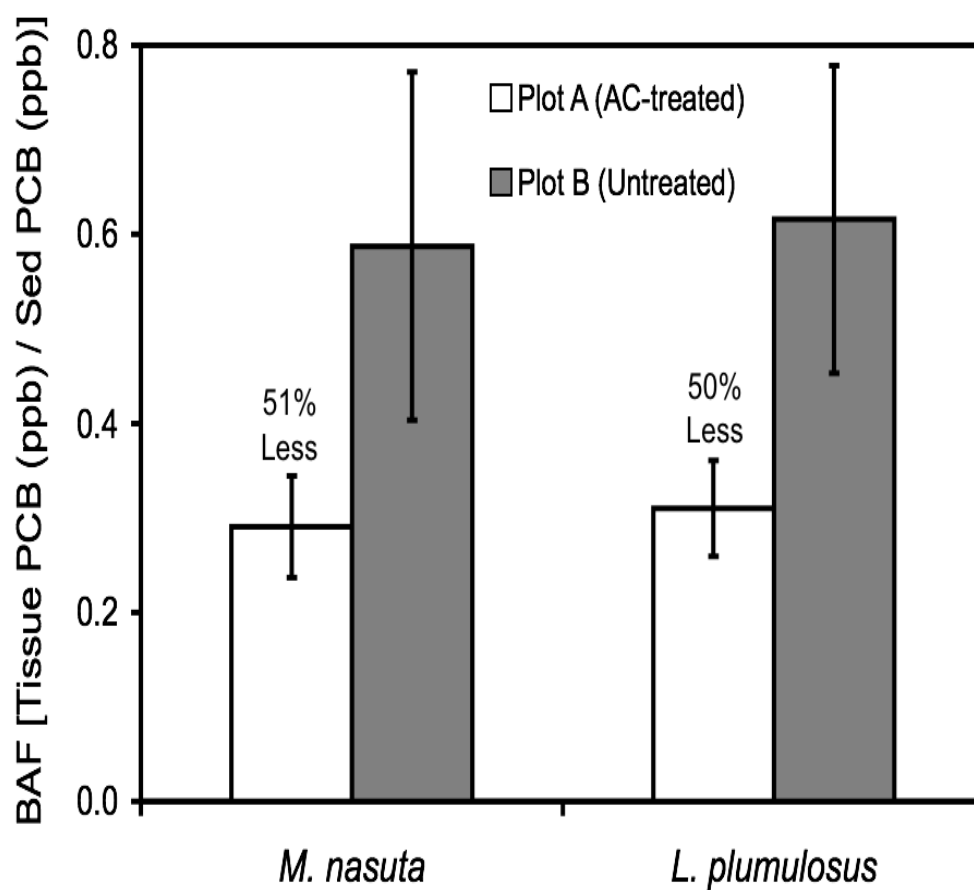


Fig. 8

